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A Contribution to the Knowledge

of

Dicarbonyl Cuprous Chloride

Dissertation

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The present work was undertaken at the suggestion of Prof. Ramsay and his constant interest and advice have been of the greatest value.

I wish to thank him most sincerely for instruction received both in the lecture-room and laboratory; I feel especially indebted to him for the high ideals, not of chemistry alone but of life as well, which I have come contact with him. Cannot fail to observe.

My thanks are also due to Profs. Heath and Clark and Dr. Matthews for the instruction received at their hands.

A Contribution to the Knowledge of Dicarbonyl Cuprous Chloride

Introduction

In attempting to determine the free oxygen in illuminating gas by means of an ammoniacal solution of cuprous chloride, Leblanc & Stas and Doyère observed that very large amounts of carbon monoxide and ethylene were also absorbed.

Leblanc then made an investigation as to the absorption of carbon monoxide by cuprous chloride and found that carbon monoxide is absorbed by a

(1) Compt. rend. (1850) 30, 483

hydrochloric acid solution of cuprous chloride with about the same facility that carbon dioxide is absorbed by caustic potash; however, in the former instance the temperature of the solution is only very slightly elevated. He also observed that an ammoniacal solution of cuprous chloride absorbs carbon monoxide, in the absence of air, to exactly the same extent as does the hydrochloric acid solution, the proportion of carbon monoxide to cuprous chloride being, as he thought, 1:1 in both cases.

He also found that the hydrochloric acid solution of cuprous chloride, saturated with carbon monoxide, could be diluted with water

to a considerable extent without any precipitate being formed, just as before the absorption, and by the dilution no evolution of gas is caused.

The same was found true for alcohol though ether seemed to decompose the compound to some extent.

Dr Blanc also noticed that by elevating the temperature or removing the atmospheric pressure, the carbon monoxide is given off as such from the solution. He did not succeed in isolating a definite compound and performed no other experiments with the solution.

He did discover however that ammoniacal solutions of the cuprous

salts in general possess the ability to absorb carbon monoxide.

It thought the absorption of carbon monoxide by cuprous chloride was to be compared to the absorption of nitric oxide by ferrous sulphate.

It was especially emphasized that this absorption might furnish evidence in support of the radical theory, which occupied the minds of chemists so generally at that time. Since cyanogen also is absorbed by a hydrochloric acid solution of cuprous chloride, he reasoned that in the chloroformic ethers ($CO\langle^{Cl}_{OR}$) carbonyl chloride ($CO\langle^{Cl}_{Cl}$) the carbon monoxide plays the part of a radical, just as does cyanogen

cyanogen chloride (CN.Cl).

In 1856 Berthelot[1] succeeded in isolating the compound formed by the action of carbon monoxide on cuprous chloride in hydrochloric acid solution. His method of preparation consisted in passing a stream of carbon monoxide through the cold saturated solution of cuprous chloride, which was repeatedly shaken to facilitate absorption. In this way he obtained beautiful pearly crystals, which attend very rapidly in the air, making it impossible to prepare them for analysis without at least some loss of carbon monoxide. The figures obtained by his analyses approximated those required by the formula

[1] Ann. chim. phys. [3] 46, 458

$7\,Cu_2Cl_2.\,3\,CO.\,7H_2O$, but since the compound alters so rapidly, he believed it to be $Cu_2Cl_2.\,CO.\,2H_2O$, and this is the composition usually ascribed to the compound, when any at all is given.

Evidently this formula is based upon very unsatisfactory evidence and the present work was undertaken to determine more accurately, if possible, the composition of the substance, to study its conduct under different conditions of temperature and pressure, and to determine the chemical activity of the carbon monoxide at the moment of its liberation.

Preparation of Material.

Cuprous Chloride.

This was prepared by the action of aqua regia on copper turnings - the latter being in excess. In the preparation about half a litre of concentrated hydrochloric acid was poured into a flask containing about 300-350 grams of copper turnings, and the acid heated almost to boiling. Then concentrated nitric acid was added from time to time, only small amounts being used in order that the solution might not boil over.

After being heated for about half an hour, the hot concentrated solution was quickly filtered through an asbestos filter, and to the filtrate cold water was added, the solution being

diluted considerably. Four or five litres of water must be added to one litre of the acid solution to cause complete precipitation of the mercurous chloride. Obtained in this way it is a fine, perfectly white powder, and can be easily filtered off and washed free from acid; but in order that the material may not be oxidized by contact with the air, it is necessary to keep enough water in the funnel to cover the mercurous chloride. The final washings were made with glacial acetic acid, and the material dried in an air-bath, at a temperature of 115°-125°C, for 12 hours.

Proceeding in this way, it is possible to obtain the material free

perfectly dry and without any alteration in color, and a specimen kept for more than six months in a glass-stoppered bottle was still perfectly white. However, it must be dried immediately after washing with acetic acid + the heating must be continued for several hours after the odor of the acid has disappeared, - otherwise it will invariably turn green in a short while, no matter how carefully it may be stoppered.

In powdering the material it is well to protect the mouth and nose, as the finely divided cuprous chloride acts as a painful irritant to the mucous membranes.

The analysis of the material gave the following results.

I 0.2012 grams material gave 0.1607 gr CuO

II 0.2112 grams material gave 0.1692 gr CuO

Calculated for

Cu_2Cl_2 (II)

Cu = 64.06%

Found

I. 63.72%

II. 63.94%

Preparation of Carbon Monoxide.

The carbon monoxide used in almost all the experiments was prepared by the action of concentrated sulphuric acid on potassium ferrocyanide. The gas was passed through four or five wash-bottles containing concentrated potash solution until on testing the gas it was found to contain practically no air, and was then collected in a glass gasometer

In all the calculations given here in the following atomic weights have been used:

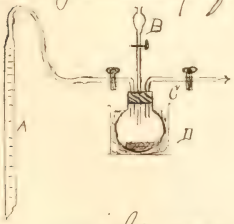
H = 1 C = 12 Cu = 63.3

O = 16 Cl = 35.5

made slightly alkaline.

The carbon monoxide obtained in this way was entirely free from carbon-dioxide and sulphur dioxide, and contained not more than 0.2 of 1% of air, and this slight amount of air came no doubt from that which was dissolved in the water used in the gasometer.

Preparation of Dicarbonyl Cuprous Chloride.



In all cases the same general method was employed. The cuprous chloride was placed in a small balloon flask (D), which in turn was immersed to a given point in ice water. The flask was tightly fitted

with a three hole rubber stopper, through one opening was passed a small dropping-funnel (B) and through the other two glass tubes bent at right angles - one of which was connected with a gas burette (A), the other (C) with a suction-pump.

After the introduction of the cuprous chloride and the immersion of the flask in ice-water, connection was ~~was~~ made with the pump and the flask evacuated - the tube leading to the gas burette having been closed. After the evacuation the stop-cock C was closed and enough hydrochloric acid introduced through the dropping-funnel to make a thin paste with the cuprous chloride. The tube leading to the gas burette, which contained the carbon monox-

etc., was then opened and the absorption flask alternately shaken and immersed in ice-water.

At first the absorption is quite rapid, but toward the end of the operation it becomes very slow and constant shaking is necessary; even then it is only after several hours that the absorption is complete. If at any time the paste in the flask became too thick to be shaken easily, more hydrochloric acid was introduced; not in excess, however, for both the cuprous chloride and dicarbonyl cuprous chloride are soluble in an excess of the acid, and I found it almost impossible to get the latter out of this solution in good shape.

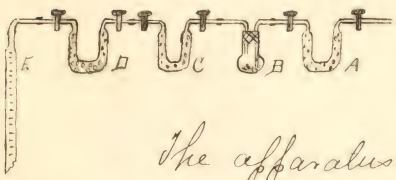
By the above process it is

possible to obtain the compound in beautiful pearly flakes, the crystals seemingly being perfectly pure - and in any quantity desired. By adding ice-water to the solution the crystals can be filtered and washed free from acid, and after some experience they can be fairly well dried between sheets of drying-paper; however, the paper should previously be cooled and the process should be applied with a previously cooled spatula. Exposure of the crystals to the air at the room temperature, for more than a minute or two, causes the entire mass to become intensely green and carbon monoxide is given off

Analysis of the Compound

I Decomposition Method.

From what has been said it is evidently impossible to dry and then weigh the compound for analysis. In the first instance it was attempted to dry the compound as quickly and thoroughly as possible, every precaution being taken to prevent decomposition, and then to decompose the compound by elevating the temperature, the products being either measured or weighed.



The apparatus consisted of a small bulb (B), of about 6 cc. capacity, into which the compound was put-

duced for the decomposition. This was provided with a tight-fitting, two-hole rubber stopper; through one opening was passed a small glass tube, bent at right angles, which extended to the bottom of the flask and was connected with a calcium-chloride tube; This was closed during the decomposition.

Through the other opening was passed a similar glass tube which extended just through the stopper and was connected with a calcium-chloride tube (C), to be used for collecting the water given off from the compound by its decomposition. This tube was protected by another calcium-chloride tube (D), the latter being connected with a gas-measuring tube (E) in which the carbon monoxide was to be col-

lected and measured. During the decompositions the little bulb containing the material for analysis, (B), was immersed to a given mark in a water bath maintained at 80°C, and blank determinations were previously made to ascertain the correction to be applied to the volume of the carbon monoxide collected, the correction being for the expansion of the gas in the bulb.

In making the determinations the compound was first boiled as previously described, washed free from hydrochloric acid by means of ice-water and quickly transferred from the Witt plate, on which it was washed, to drying-paper, pressed between folds of the paper with a cold spatula

transfrred from one spoon to another, until on pressing with a cold glass tube a moist [illegible] was made on the drying-tube.

This operation did not require more than one minute, and none but cold objects should touch the crystals, otherwise they immediately become green. Just as soon as dry, the crystals were quickly placed in the decomposition-bulb (H), which had been previously weighed, the stopper fitted in tightly and connection made with the weighed calcium-chloride tube (C), which must retain the water given off by the compound; the connections with the second calcium-chloride tube (D) and the gas-measuring tube (E) were [illegible] as the same

tance. The decomposition-bulb was then immersed to the mark in the water bath and a temperature of 80°C maintained until there was no further change in the volume of gas in the measuring-tube (E), and this volume was read, corrected for temperature, pressure, and water vapor, the correction due to the expansion of the gas in the decomposition-bulb being also applied. In this way the volume of carbon monoxide given off from the compound was ascertained.

Of course only a small portion of the carbon monoxide given off ever reached the measuring-tube, but the air displaced was measured; accordingly can was

to have the pressure in all parts of the apparatus the same and equal to the atmospheric pressure, before the final readings of the gas volume were made.

The volume of the carbon monoxide having been ascertained, the measuring-tube was disconnected and dry carbon-dioxide passed through the calcium-chloride tube A, and through the decomposition-flask, the latter remaining in the water-bath at 80° C. In this way the material analyzed came to thoroughly dried and the current of gas was continued until there was no further change in the weight of the bulb. Then the bulb and drying calcium-chloride tube were again

carefully weighed, the difference between the first and last weighings being the weight of cuprous chloride and carbon monoxide respectively; the total weight of the constituents, obtained by the decomposition of the compound being known, the percentage of each constituent was calculated.

The cuprous chloride remaining in the decomposition-bulb was always found to be slightly green in color. This seemed due not to the action of the carbon dioxide, but to oxidation by the air in the bulb when the compound was introduced. In order to obviate this difficulty a bulb as small as possible was employed and by analysis the cuprous chloride

was found to be within about .05 of 1% pure.

While this method is theoretically very simple, it is in practice almost impossible to obtain concordant results by means of it. The great difficulty is the extreme instability of the compound in contact with the air, making it almost, if not quite, impossible to dry it without loss of carbon monoxide and oxidation of the cuprous chloride. A large number of analyses were made in this way, but the results were not satisfactory, even after considerable skill had been acquired in drying and handling the precipitate, and the method was finally given up for a still simpler one

However this was the only method used by means of which it was possible to determine the percentage of water, and while I would place rather small faith in this method alone, yet, supported as it is by the more accurate method the results do have a certain value - a value that can enable one to ascertain with a fair degree of accuracy the amount of water in the compound.

Below I give the results of three analyses, four specimens of the first made, though others showed even greater variations than these

Determination No. I.

Weight	Cu_2Cl_2	= 0.3280 gr.	= 60.78%
"	H_2O	= 0.1220	= 22.61%
"	CO	= 0.0896	= 16.60%
	Total	= 0.5396	99.99

Or calculated only for cuprous chloride and carbon monoxide, we have

(1) Weight Cu_2Cl_2 = 0.3280 gr. = 78.54 %
" CO = 0.0896 = 21.45 %
Total 0.4176 99.99

Determination No. II.

Weight Cu_2Cl_2 = 0.2180 gr. = 62.21 %
" H_2O = 0.0740 = 21.11 %
" CO = 0.0584 = 16.67 %
Total = 0.3504 99.99

Calculated in terms of Cu_2Cl_2 and CO.

Weight Cu_2Cl_2 = 0.2180 gr. = 78.87 %
" CO = 0.0584 = 21.13 %
Total = 0.2764 100.00

(1) The results are also expressed in terms of these constituents for the purpose of comparison [illegible]

Determination No III.

Weight Cu_2Cl_2	= 0.2170 gr	= 62.41 %
" H_2O	= 0.0750	= 21.57 %
" CO	= 0.0557	= 16.02 %
Total	= 0.3477	100.00

Calculated in terms of Cu_2Cl_2 and CO.

Weight Cu_2Cl_2	= 0.2170 gr	= 79.31 %
" CO	= 0.0557	= 20.42 %
Total	= 0.2727	99.99

II Absorption Method.

Finding that it was impossible to obtain sufficiently accurate results by the method just described, it was decided to take a known quantity of cuprous chloride and determine the amount of carbon monoxide it would absorb. The apparatus used in the

same as that employed in the preparation of the compound and described on page 11. From one to two grams of cuprous chloride was carefully weighed and introduced into the absorption-bulb (D), which was then closed, immersed in the mark in ice-water and exhausted. The exhaustion being complete, the connection with the pump was closed, enough concentrated hydrochloric acid introduced to form a thin paste with the cuprous chloride, the connection with the gas-measuring tube opened and carbon monoxide allowed to enter, the volume of gas in the tube being quickly noted as soon as atmospheric pressure is reached in the absorption-bulb. The bulb was then alternately shaken and

dipped in ice-water until no more carbon monoxide could be absorbed. This requires from two to three hours. Toward the end the absorption is extremely slow, and almost constant shaking is required so that the unchanged cuprous chloride may be exposed. Also care must be exercised that the material does not stick to the sides of the bulb, else some of the unchanged cuprous chloride will be covered by the dicarbonyl cuprous chloride, and so complete absorption be prevented. It is needless to say that the absorption was made as complete as it was possible to get it. In some cases the absorption-bulb was kept in ice-water for several days, being shaken at intervals, but no

was absorbed after one hour, three hours, four & five hours, when the operation had to cease the former treatment

It was only after 2 months work, in which time at least fifty determinations were made, that I could obtain concordant results, the most likely to incomplete absorption. All previous determinations were then discarded and a new series of about twenty-five made, in which the results varied by only a few tenths of one per cent.

Determinations were also made to see if the strength of acid used had any influence on the amount of Carbon monoxide absorbed. It was found to have no effect at all, only that the absorption was more

rapid. The more concentrated the acid used — due, no doubt, to the greater solubility of both compounds in the stronger acid.

These results led me to try pure water instead of hydrochloric acid, and, while the absorption is very slow yet in fact by the same amount of carbon monoxide is absorbed as when the acid is used. This fact has never been noticed before, and since the same amount of gas is absorbed and the appearance of the crystals is identical in all cases, it tends to show that when hydrochloric acid is used as a solvent none of the acid enters into the composition of the compound.

When the bulb containing carbonyl cuprous chloride is heated

to 60° or 70°C, exactly the same amount of carbon monoxide is given off as was absorbed in the first instance. on cooling the bulb it is exactly reabsorbed and this operation can seemingly be repeated indefinitely. Dry cuprous chloride does not absorb dry carboy monoxide.

I give below four analyses in the order in which they were made.

Liter No IV. Solvent H_2O

Weight Cu_2Cl_2 = 2.000608 gr.

∴ CO absorbed = 0.54374 c.c.

CO = 21.37%

Liter No V. Solvent 1 part HCl to 4 parts H_2O

Weight Cu_2Cl_2 = 1.007507 gr.

∴ CO absorbed = 0.27031 c.c.

CO = 21.20%

a In all cases when the weights or volumes of gases are employed, the corrections for temperature, pressure and water vapor have been applied

Deter. No. VI. Solvent, conc. HCl + 2 parts H_2O

Weight Cu_2Cl_2 = 1.00690 gr.

" CO absorbed - 0.27332

$CO = 21.35\%$

Deter. No VII. Solvent conc. HCl

Weight Cu_2Cl_2 = 1.00270 gr.

" CO absorbed - 0.27487

$CO = 21.51\%$

I am aware that there is one considerable source of error in this method. The compound formed, as well as the cuprous chloride, is insoluble in water and only slightly soluble in hydrochloric acid, so that in making [illegible] The absorption is continued very vigorously the bulb is shaken until unchanged cuprous chloride will

Always 2 molecules of the dry cuprous chloride formed and the results obtained in this way were invariably a slightly low.

As regards the formulæ expressed by these results - Erlandsen gives the percentages of carbon monoxide required by different formulas

$Cu_2Cl_2 . CO$; $CO = 12.41\%$

4 $Cu_2Cl_2 . 7CO$; $CO = 17.91\%$

5 $Cu_2Cl_2 . 9CO$; $CO = 20.37\%$

6 $Cu_2Cl_2 . 11CO$; $CO = 20.66\%$

12 $Cu_2Cl_2 . 23CO$; $CO = 21.40\%$

$Cu_2Cl_2 . 2CO$; $CO = 22.13\%$

It is evident that the formula considered probable by Erlandsen $Cu_2Cl_2 . CO$ and the one suggested by the experiments by Berthelot ($Cu_2Cl_2 . CO . 2H_2O$) [illegible] for

in Tabelle since the percentage of carbon monoxide in $Ag_2.CO$ is only 12.4; the average in my determinations is about 2.4%.

Exactly 2.4% of carbon monoxide is required by the formula $12 Ag_2.2CO$; while such complex compounds are not unknown in inorganic chemistry, certainly they are quite rare, and while the percentage of carbon monoxide required for $Ag_2.2CO$ is 22.13%, about 0.7% higher than the average found, at the same time it must be borne in mind that in both methods used there is a constant error causing the percentage of carbon monoxide to be too low, so that it seems not fair to accept the proportion $Ag_2.2CO$ as rigidly demonstrable.

As regards the proportion of water contained in the compound we must rely on the "decomposition method". As stated on page 23, this method was found quite unsatisfactory, for in practice the range of error must be certain monoxide as determined in this way. (CO = Deter. No I = 21.45%; No II = 21.13%; No. III. = 20.42. These results show that while the compound has decomposed slightly, yet the average percentage of carbon monoxide (2.0%) is only slightly below the average obtained by the other method (21.4%). As previously stated, 2 units are supposed to be assuming the proportion $Fe_2O_3 \cdot 2CO$ established. Assuming this proportion of the compound constant and varying the proportion of water, we obtain:

$Cu_2Cl_2.2CO.3H_2O$; $H_2O = 17.35\%$

$Cu_2Cl_2.2CO.4H_2O$; $H_2O = 22.11\%$

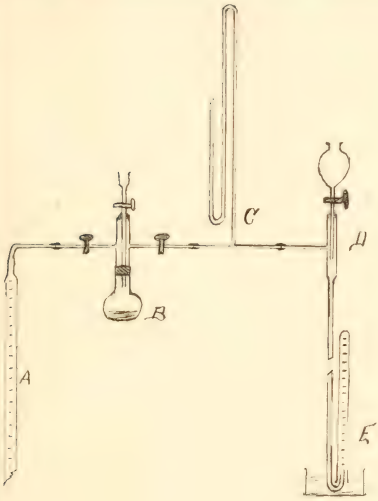
$Cu_2Cl_2.2CO.5H_2O$; $H_2O = 26.17\%$

The average percentage of water as determined by the "decomposition method" (page 23) was seen to be 21.76%, being only 0.35% lower than required for $Cu_2Cl_2.2CO.4H_2O$. On the other hand it was 4.2% higher than required by $Cu_2Cl_2.2CO.3H_2O$, and 4.43% lower than required by $Cu_2Cl_2.2CO.5H_2O$. Considering these facts, it seems highly probable that the composition of dicarbonyl cuprous chloride is expressed by the empirical formula $Cu_2Cl_2.2CO.4H_2O$.

Behavior of Dicarbonyl Cuprous Chloride under Reduced Pressure

As was recognized by Leblanc, this compound loses carbon monoxide when the atmospheric pressure is removed. No exact statement has ever been made as to the pressure at which the decomposition begins, accordingly experiments were undertaken to ascertain just how the compound conducts itself when the pressure is removed.

In the preparation of the compound exactly the same precautions were observed as previously described, the apparatus used being modified in the following manner.



The compound was prepared in a small bulb B of about 5cc capacity. The bulb was provided with a dropping funnel, of special design as shown, which could be disconnected or connected with a gas-measuring tube A, and also a Sprengel pump at manometer C was connected with the tube leading to the pump

Blank experiments were made to ascertain the correction, on account of the expansion of the air in the bulb & tubes, which must be applied in the determinations. For this purpose the flask, containing the same amount of water used in the actual experiments (30°), was immersed to the mark in ice-water, and the pump started. The gas pumped out at the different pressures was collected in the measuring tube (E), & corrected for temperature, pressure and water vapor. These corrections are

Pressure	Vol. air collected	Pressure	Vol. air collected
460 mm.	29.9 cc.	130 mm.	60.0 cc.
360 "	39.0 "	100 "	63.2 "
260 "	48.2 "	60 "	66.4 "
160 "	57.6 "	40 "	68.0 "

The compound having been prepared in the usual manner it was only necessary to close the top mercury with the gas burette and open the stopcock leading to the pump.

In the first series of experiments dilute hydrochloric acid (1 part acid to 12 parts water) was used and the tabulated results are given below.

Determination No. 1. Solvent $1HCl + 12H_2O$

Weight Coeg Cl_2 = 0.505809 gr.

" CO absorbed = 0.13644 " = 109.0 cc

CO = 21.24%

Pressure Height Hg. in mm.	Total vol. gas	Correction	CO given off	% Decomposition
500 mm	27.99 cc.	27.9 cc	0.07 cc	.07%
400 "	39.40 "	37.0 "	0.40 "	0.35%
500 "	49.20 "	48.2 "	1.00 "	0.81%
600 "	59.80 "	57.6 "	2.20 "	1.92%
625 "	170.16 "	57.3 "	111.86 "	98.13%
720 "	182.01 "	68.0 "	114.01 "	100.00%

for every difference of 100 mm in pressure. The apparatus was allowed to stand 24 hours, to see if the height of the manometer remained constant. This was the case until 635 mm (35 mm pressure) was reached; while occasional bubbles of gas had been giving off during the action of heating, the bubbles now became so numerous that the liquid appeared to be boiling. The pressure varied between 135 - 12. mm for each, each time the manometer was raised higher it rose back to this pressure and no more, but at the end of the time it became constant, and so tabulated above the amount of gas collected was 111.86 cc or 2.75 cc more than was absorbed at first. The pressure being still further reduced from 135 mm to 40 mm only 2.15 cc of

gas ... given off, showing first point of decomposition ... approximately 130 mm pressure and the decomposition ... practically complete at that point.

Decomposition of H_2O II. Solvent, 1 part H_2O to 2 parts H_2O

Weight Exp Cl_2 - 0.4710 gr.

∴ CO absorbed 0.1317 gr. - 105.51 cc

CO = 21.17%

Pressure	Total Vol. gas	Correction	CO Given off	% Decomposition
460 mm	30.2 cc	29.9 cc	0.3 cc	0.28%
360 "	39.4 "	37.0 "	0.4 "	0.37%
260 "	49.5 "	48.2 "	1.3 "	1.21%
160 "	57.6 "	55.6 "	2.0 "	1.81%
135-125 "	165.6 "	59.5 "	106.3 "	77.42%
40 "	174.7 "	68.0 "	106.7 "	100.00%

Three ... decompositions ... gases.

experiments, the first being especially poor, the last being slightly better than the average. In all cases more gas was collected than the amount of Carbon monoxide plus the correction to be applied but I think one can easily understand this error when it is noted that not all rubber connections could be dispensed with, owing to the necessity of shaking the bulb during the passage of Carbon monoxide - though these connections were kept well coated with shellac. However, it hardly seems possible that the should have entirely prevented leakage through the rubber, assuming that all the stop cocks were properly ground, for each experiment extended over a half hour's work, and for the most part a very low pressure was maintained in the

The decomposing-bulb was kept in ice-water all the time, and of course it was a matter of considerable difficulty to maintain an accurately constant temperature during the period.

Considering these three little sources of error, I think we can overlook the various things observed, and it seems quite evident that the compound is decomposed in this way, as when silicic hydrochloric acid being used, there is not decomposition until the pressure is reduced to 135-145 mm, and that it is complete by decomposed at this point.

Action of the compound on moist silver.

The compound obtained by the decomposition of carbon monoxide on cuprous chloride in water was next treated

to reduced pressure at 0°C and quite unexpected results were obtained.

Experiment No. I

CO absorbed = 90.05 c.c.

Pressure	Total Vol. Res.	Correction	CO Given Off	% Decomp.
460 mm	30.1 cc	29.9 cc	0.2 cc	0.22
360 "	37.3 "	37.0 "	0.3 "	0.33
260 "	49.0 "	48.2 "	0.8 "	0.88
160 "	38.8 "	37.6 "	1.2 "	1.32
130 "	102.7 "	60.0 "	42.7 "	46.97
100 "	107.2 "	63.2 "	45.1 "	50.21
60 "	156.7 "	66.4 "	90.5 "	99.55
40 "	158.7 "	68.0 "	90.7 "	100.66

By way of explanation: on lowering the pressure from 160 mm to 160 mm only 1.2 cc of carbon monoxide were given off, but at 130 mm pressure the quantity

gas became quite vigorous, and when the pressure was lowered it rose again to this point and stopped. This was continued for about five days when 42.7 cc of carbon monoxide had been given off, and when the pump was started the mercury rose quite rapidly and I believe the pressure of 130 and 60 mm. was very nearly 0 cc. If gas was given off. However at about 60 mm pressure the evolution of gas seemed to increase and the total volume given off up to and including 60-65 mm was 70.5 cc. But 42.7 cc was given off at 130 mm, so 5 cc. believe, 130 + 60 mm, so the volume given off below 60 mm pressure = 70.5 cc - (42.7 + 5 cc) = 42.8 cc. The total volume given off was 70.7, so that almost exactly half was given off at 130 mm and the remainder at 60 mm pressure.

Considering the coarse reading by gases worked with and the fact that the two points of decomposition are quite sharp and very close together, being 130 and 60 mm respectively, namely during the low temperature employed and the great length of time required, I think, any one will agree that the figures are not altogether a rough estimate of about correct.

E. formed H2O.

Assume, a comparison value, being used, gun results as follows:

CO (boiled) - 103.33°

Pressure	Total Vol Gas	Correction	CO Given Off	% Decomposition
460 mm	30.2 cc	29.9 cc	0.3 cc	0.28
360 "	39.5 "	31.0 "	0.5 "	0.3
260 "	49.2 "	48.2 "	1.0 "	0.75
160 "	57.0 "	55.6 "	1.4 "	1.33
130 "	109.91 "	60.0 "	41.91 "	41.70
100 "	114.92 "	63.2 "	51.72 "	41.35
60 "	170.81 "	66.4 "	104.41 "	99.63
40 "	172.81 "	68.0 "	104.81 "	100.00

Total vol. gas collected = 104.81 cc
" " " absorbed = 103.33 "
Difference 1.54 "

½ Vol gas absorbed = 51.66 cc
Vol. gas given off at 130 mm = 41.91
Difference 1.67

I have noted during the decomposition by electric discharge, of the compound as made with the use of water, that the cuprous chloride left in the decomposition bulb was quite dark, due to an admixture of dark particles, and there was also a very fine dark coating on the bottom of the bulb. It was not possible to tell with certainty what the material was, the quantity being too small, but it certainly contained copper for the part detached to the bulb was carefully washed and dried, in appearance it was exactly like the coatings of metallic copper formed by the precipitation from clear and in fine condition. The fact is mentioned here since it may furnish an

explanation of the formation of carbon dioxide when oxygen acts on dicarbonyl cuprous chloride.

Behavior of the Compound as made with Concentrated Hydrochloric Acid

Inasmuch as the conduct of the compound made with water differs from that made with dilute hydrochloric acid, it was deemed necessary to test the behavior under reduced pressure of the compound made with concentrated acid. The following example will suffice to show the results in a general way.

Solvent conc. HCl. Temperature 0°C
Vol. CO absorbed = 105.2 cc

Pressure	Total Vol. gas	Correction	CO_2 given off	% composition
710 mm	40.7 cc	37.2 cc	1.5 cc	1.38
310 "	60.2 "	44.7 "	15.5 "	14.32
260 "	57.4 "	48.2 "	26.2 "	24.21
210 "	71.8 "	52.7 "	38.7 "	36.75
160 "	117.2 "	51.6 "	37.6 "	35.08
130 "	168.5 "	60.0 "	108.2	100.0

It will be seen from the above that in this instance decomposition begins at a pressure of about 710 mm and gradually increases as the pressure is lowered to 160 mm; from 160 to 130 mm the decomposition is markedly increased and at 130 mm is complete.

This decomposition agrees with those in which dilute acid was used in that decomposition is complete at 130 mm pressure; it differs from both the

others in that [illegible] pressure varies
regions below 150 mm. The stronger the
acid the greater [illegible] ease with which
Carbon monoxide is absorbed by cu-
prous chloride and the greater the
ease with which this gas is again
given off under the influence of re-
duced pressure.

Experiments in which other strengths
of acid were used were not under-
taken for each experiment extends
through [illegible] three weeks, the bulb
containing the compound must be
kept [illegible] in use all this time,
and to maintain a given pressure
requires almost constant attention.
Further, the slightest leak in apparatus
or connections will cause loss of vacuum
a pressure of only .5 - 140 mm is maintained

for several months, and by course the slightest leak means absolute loss of the experiment. On account of experimental difficulties it was not found desirable to take readings at room temperature - would repeat for some time.

These results will later be discussed in detail and the decomposition tension be expressed in the form of curves.

Absorption of Carbon Monoxide by Cuprous Chloride in Pyridine.

It was desired to test the effect of increased temperature upon a compound of cuprous chloride and carbon monoxide. Since the compound formed by the absorption of CO by cuprous chloride in water or hydrochloric

acid is to convert it into [illegible] to prevent the accurate study of the dissociation by means of [illegible].

W. Lang[1] has shown that cuprous chloride in pyridine has the power of absorbing carbon monoxide and the work was undertaken in the hope that a compound might be obtained which would form more stable towards heat than the one first studied, but the [illegible] was found to be the least stable.

The general method of procedure was the same as that described on page 11, except that the water and acid were replaced by pyridine. One peculiarity was noted; as water from completely the bulb was removed, the resistance of the pyridine came in contact with the cuprous chloride [illegible]

[1] BEr. 21, 1584

assumed a deep green color, due probably to some product of oxidation. The flask also became warm on account of the reaction between the two compounds, and the cuprous chloride exhibited a great tendency to form small hard lumps. It was necessary in every case to heat to 60 or 70° in order to get these lumps broken up and into solution, and it was very difficult to tell whether some particles were not still suspended, so the solution was boiled for a few minutes. [illegible] possible, the bulb was vigorously shaken & immersed in ice-water until the whole cuprous chloride could be absorbed; in the [illegible]

The operation the chloride [illegible] extremely slow.

Various attempts were made to isolate the compound formed, and finally on adding to the mixture, the stopper being ground in, a beautiful white plate on the bottom of the bulb, but all these attempts failed utterly. On the addition of water to the mixture, much of the compound [illegible] in the form of flakes and when an attempt is [illegible] these off they [illegible] instant the air touched them. So much more unstable in the air is this compound than the one made by the use of water or hydrochloric acid, that an attempt to dry [illegible] would [illegible]

[illegible]

added to the pyridine solution and there is volume of 30% alcohol in the mixture allowed to stand undisturbed for several hours. The color of the solution became very little intensely green, and gradually there were deposited minute crystals, similar in appearance and as reported to the compound described by Lang[1], to which he assigned the formula $(C_5H_5N)_2CuCl_2$. The compound can be easily filtered, washed and dried and under and is pure form. One analysis per other gave the following result.

0.2103 gr. Material gave 0.0705 gr. CuO

Calculated for $Cu_2Cl_2.2C_5H_5N$	Found.
Cu = 21.65%	21.61%

Working on all [illegible] to obtain [illegible]

(1) Ber. 21, 1558

formed by the absorption of carbon monoxide by cuprous chloride in ammoniacal solution, as source must be had to the Hempel method, which, of course, has called forth the determination of the absorbing return, the two constituents being monoxide and cuprous chloride.

A large number of absorptions were made and it was necessary to arrange series, though the result had rather to the higher than to the lower percentages.

Weight Cu$_2$Cl$_2$	Weight CO absorbed.	% CO.
1.0005 gr.	0.172637 gr	14.11
0.2020 "	0.035630 "	14.98
0.2055 "	0.036311 "	15.00
0.4036 "	0.072710 "	15.26
0.4028 "	0.076182 "	15.70
0.2040 "	0.039030 "	16.05

It is seen at once that the results vary quite widely, due probably to the coking of the cuprous chloride and also to the tendency of the compound to form double salts with the ammonium chloride, thereby making complete absorption impossible.

If the relation of cuprous chloride to carbon monoxide is a simple one, it is of probability $2Cu_2Cl_2.3CO$, since the percentage of carbon monoxide, as determined in the absorption method, is undoubtedly low.

The percentages required by the various hypothetical compounds are as follows -

$Cu_2Cl_2.CO$; CO - 12.41 %

$2Cu_2Cl_2.3CO$; CO - 17.57 %

$3Cu_2Cl_2.4CO$; CO - 19.10 %

$Cu_2Cl_2.2CO$; CO - 22.13 %

While this method of [illegible] and make it possible to [illegible] therein by [illegible] enters into the compound, yet [illegible] to the compounds made with water and by [illegible] alone regarding $Cu_2Cl_2.2CO.4H_2O$, one would be led to suspect that it does.

If the proportions $2Cu_2Cl_2.3CO$ are formed, and pyridine enters into the compound it might occur to one that it is derived from $2(Cu_2Cl_2.2CO)$ by replacement of one CO by C_5H_5N, though there is no evidence whatever on the point.

Behavior of the Compound under Elevated Temperatures.

The method of work was the following. Into a tube of [illegible]

was nitrated a weighed quantity of
pure zinc chloride (about 0.4 gm.) and
the bulb closed with a two-hole rubber
stopper, through one opening was passed
a dropping funnel and through the
other a bent glass tube. The bulb was
then alternately exhausted and filled
with nitrogen until it was completely
filled with this gas; 5 cc of pyridine
was accurately measured and introduced
through the dropping-funnel, the
bulb was connected by means of rub-
ber tube with a gas burette, and the
bulb immersed in a glass vessel of
water bath, the temperature of which
was accurately regulated.

The temperature of the bath was
gradually increased, readings being
made at the desired points.

making the final readings of the volume of gas in the burette, and the pressure of the gas in the bulb by equalization of the levels of the mercury columns, in order that the volume might be absolutely constant. In this way a series of corrections was obtained, which were applied in the actual determinations. The corrections used, the average of several series, were as follows:

Temp of bath	Vol gas collected	Temp of bath	Vol gas collected
0° C	0.000 cc	60°	8.592 cc
10°	1.869 "	70°	10.863 "
20°	2.849 "	80°	13.578 "
30°	3.917 "	90°	16.739 "
40°	5.164 "	100°	21.401 "
50°	6.767 "		

... would be noticed the volume of gas collected above 100 would increase rapidly, especially as the temperature of the boiling point of the liquid was approached, also the pressure at the surface. The rubber stopper and connections of this form retain gas and there may be a small error on this account.

In the volume experiments it was always impossible to get off as much gas as was absorbed; this was explained no doubt, by the difference in the vapor tension of pyridine containing dissolved chloride and pyridine containing the corresponding dissolved bromide compound. Indeed the reaction between the pyridine and rubber connections at this rather elevated temperature, or the pyridine and cuprous chloride, or

this latter and carbon monoxide, or in the case of these compounds, may have affected slightly the readings obtained.

It is worthy of notice that after each decomposition the bulb contained a coating of what seemed to be metallic copper and which gave the test for copper. The coating was more abundant than that noticed in the decomposition by the corresponding chloride by pyrogallic acid. It is conceivable that the following reaction had taken place-

$2Ag_2Cl_2 + CO \rightarrow 2Ag + COCl_2$ and then

$COCl_2 + H_2O \rightarrow 2HCl + CO_2$.

If this was really the case by means the certain reagents passed in through in the water in the gas bottle, the having the readings slightly lowered.

In all these experiments the components

was expended in removing the
the decomposition was added exactly as
in the blank experiments.

Decomposition No. I.

Weight Ag_2O = 0.4036 gm.

" Oxygen = 0.0424 = 38.144 cc

CO = 15.56 cc

Temp.	Total vol gas	Correction	CO_2 by KOH	CO_2 by combustion
10°	2.711 cc	1.867 cc	0.845 cc	1.45
20°	12.858 "	2.847 "	11.00 "	18.13
30°	22.283 "	3.111 "	18.366 "	31.55
40°	31.188 "	5.164 "	26.037 "	44.15
50°	40.012 "	6.167 "	33.245 "	57.11
60°	47.365 "	8.312 "	38.113 "	65.02
70°	54.511 "	10.96 3"	43.105 "	75.11
80°	61.207 "	13.278 "	47.621 "	81.16
90°	68.824 "	16.137 "	52.083 "	89.07
100°	76.021 "	21.401 "	54.625 "	92.75

Decomposition No II.

Weight Au_2Cl_2 = 0.40428 gr.

" CO absorbed = 0.0702" = 56.1576 cc

CO = 14.xx%

Temp	Total Vol. gas	Correction	CO given off	% composition
10°	4.016 cc	1.869 cc	2.147 cc	3.82
20°	11.847"	2.847"	9.000"	16.02
30°	23.138"	3.117"	11.221"	37.22
40°	28.158"	5.164"	22.994"	40.94
50°	37.015"	6.767"	32.248"	57.42
60°	41.134"	8.372"	37.342"	66.05
70°	53.951"	10.863"	43.088"	76.72
80°	61.831"	13.578"	48.253"	85.92
90°	68.042"	16.737"	51.303"	91.35
100°	77.515"	21.461"	53.194"	94.71

Decomposition by No III.

Weight Cu_2Cl_2 = 0.402809 gr.

" CO absorbed = 0.07618 = 60.1216 cc

Cl = 15.10 %

Temp	Total vol gas	Correction	CO given off	% decomposing
20°	12.279 cc	2.847 cc	7.400 cc	13.42
40°	32.370 "	3.164 "	27.206 "	44.65
60°	47.872 "	8.392 "	37.300 "	64.31
80	64.043 "	13.578 "	50.465 "	82.83
100°	77.326 "	7.401 "	56.195 "	92.12

Curve representing these decomposition will be found on page 134.

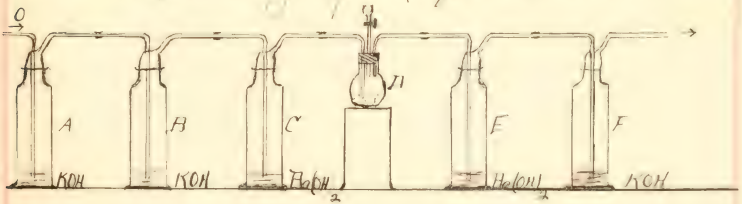
Action of Oxygen on Dicarbonyl Cuprous Chloride.

Experiments were undertaken to determine whether or not the carbon monoxide at the moment of its liberation from the complex, differs in

coal entirely from the gas in order to be sure, and also to study the rate with which it was given off when the compound is submitted to the influence of other gases.

The method of work was the following: about 500cc of carbon monoxide were absorbed by cuprous chloride just as in the preparation of ferrocarbonyl, cuprous chloride, except that the tube through which the carbon monoxide entered was long enough to reach to the bottom of the bulb into which it was sealed above.

The absorption complete, the bulb was introduced into the following system of wash bottles.



As shown, the apparatus consisted of two gas wash bottles containing strong caustic potash solution, through concentrated baryta water, and into the flask containing dicarbonyl cuprous chloride, the inlet tube reaching to the bottom of the flask. The gas on issuing from the flask passed through concentrated baryta water, which was protected from the air by a bottle containing caustic potash.

While the flask containing the dicarbonyl cuprous chloride was still immersed in ice-water, oxygen was admitted and almost instantly began to form grey and bubbles of carbon monoxide were given off. After the passage of oxygen for about ten minutes a decided coating invariably appeared on the inlet tube of the baryta bottle.

and at the end of half an hour a
Weidel precipitate had ceased, enough
to make the barium solution turbid when
shaken. The barium water in the bottle
before the decomposition flask remained
as clear as distilled water. This experiment
was repeated a number of times, always
with the same result.

Attempts were made to determine the
amount of barium carbonate, by weigh-
ing the sulphate and also titration, us-
ing phenolphthalein and methyl orange
as indicators. The amount of barium
carbonate, as compared with the barium
hydrate, was so small, that an accu-
rate determination was impossible, but
it could safely be said that the amount of ba-
rium carbonate did not represent an
oxidation of more than 1% of the dextrose employed.

Plumbic oxide must be made either
the carbon dioxide came from
the carbon dioxide or from the oxidizing of your
carbon monoxide. It could not have been
contained in the carbon monoxide for
this was carefully tested in every experi-
ment. However, only direct experiment
could test whether the supposed chlo-
ride contained any thing which might
give carbon dioxide under these condi-
tions; another possibility was that by
oxidizing the supposed chloride the oxygen
had become powerful enough actively en-
abling it to attack the rubber stopper
and connections.

Thinking that carbon monoxide
might be alternately absorbed and given
off when a mixture of this gas and oxy-
gen is allowed to pass through moist

cuprous chloride at 0°C, the following method was adopted. From 1½ grams of cuprous chloride were placed in the glass tap described, covered with water free from carbon dioxide, the flush immersed in ice-water and placed in the bore of wash-bottle as described. Pure oxygen was passed for 1½ to 2 hours, the cuprous chloride gradually becoming grey, though not so rapidly as when dicarbonyl cuprous chloride was used; the test baryta solution (E) remained absolutely clear. They without disturbing the apparatus, carbon monoxide was run in until the oxygen is equal proportions and when the mixture had been shaken for fifteen minutes in cooling again to 0°C and the exact tube of the

[illegible] of the [illegible] of two hours a perceptible precipitate [illegible] afterwards.

As one might expect the precipitate formed in this way was not so large in proportion to the carbon monoxide used as when the carbon monoxide had been previously absorbed by the cuprous chloride; each after several more hours the precipitate did not increase very markedly, due to small amount of the cuprous chloride in the oxidation products formed. These experiments were repeated over and over, and always with the same result.

I might mention here that the passage of a mixture of oxygen and [illegible] or chloride does not bring about it

formerly of any carbon dioxide.

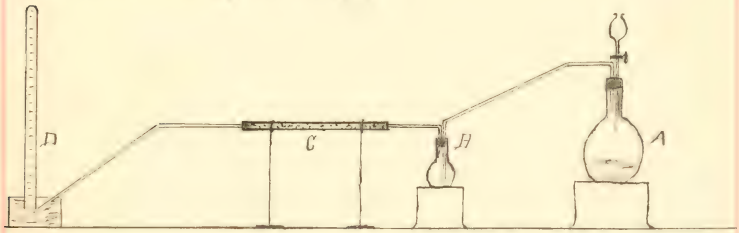
Action of Chlorine on Dicarbonyl Compounds.

If carbon monoxide at the moment of liberation from dicarbonyl cuprous chloride is in a state of activity greater than that it possesses under ordinary conditions, we certainly may expect this activity to reveal itself more markedly under the influence of chlorine, with which it unites in some case.

Accordingly, experiments were undertaken in the hope of throwing some light on this point. Dicarbonyl cuprous chloride contains water of crystallization, from which anhydrous chloride if formed, would appear as certain dioxide and hydrochloric

work. The determination of the amount of Carbon monoxide changed under these circumstances is fraught with many difficulties as a moment's reflection will show, for in the absorption of Carbon monoxide the mixed gases require shaking and at intervals must the temperature be raised or the pressure altered, neither must the compound employed take part.

The method finally adopted, and for which great accuracy cannot be claimed, was the following



The dicarbonyl cuprous chloride was

prepared in the usual manner in a bulb of known size, about 200 cc. The amount of oxygen necessary to oxidize was accurately measured. The absorption-bulb was provided with an inlet tube extending to the bottom of the vessel and an outlet tube reaching just through the stopper.

After the preparation of the compound the inlet tube was connected with a chlorine generator, in which contained an excess of chlorine as it was possible to obtain; at the same instant the outlet tube was closed. The generator was connected with the oxygen tube of about 30 cm length and containing finely divided antimony. The antimony tube was in turn connected with a gas measuring tube containing strong caustic potash.

The moment the chlorine touched the surface of the cuprous oxide crystals they turn colorless and bubbles of carbon monoxide were seen rising from them. The passage of chlorine was continued until the cuprous chloride had been oxidized and had gone into solution. The excess of chlorine was taken up by the antimony, and very certain oxychlorides formed, or any hydrochloric acid passing over, was absorbed by the caustic potash solution; the unchanged carbon monoxide passed on and was collected.

At the end of the operation the vessel (H) containing originally the ammoniacal cuprous chloride, in which it was found, was heavy, was filled with fine crystals as to be sure that all carbon monoxide

[illegible] by known [illegible]. Knowing the
amount of carbon monoxide combined
and also the capacity of the apparatus
both used hence the volume of the car-
bon monoxide contained in it after
the absorption it was only necessary to
subtract the volume of gas collected
from the sum of these two to deter-
mine the amount of carbon monoxide
that had been changed.

Blank experiments were made to
see if any hydrogen was given off from
the action of the acids on the
hydrochloric acid which might have
been dissolved in the amount of gas
then was found on many occasions
that hydrogen was evolved. It was also
determined that powdered calcium car-
bonate in the cause of operations [illegible]

returning chlorine and making impossible [illegible] of the gas as passed over it.

Although the mercury tube was filled as completely as possible and all connections made with capillary tubing; in spite also of the heat coils employed to keep all parts of the apparatus at the same temperature before and after each experiment, yet it was impossible to obtain any satisfactory result.

The rate of flow of the chlorine seemed to have some effect on the length of contact possible, being greater the slower the current, the same effect was produced by lowering the temperature, thus increasing the density [illegible] of the gas.

The greatest difficulty was experienced in obtaining perfectly pure chlorine, as a very slight trace of air would accumulate and cause a considerable error, for the chlorine had to be passed for about an hour before complete decomposition was secured.

The simplest and best method for preparing the chlorine seemed to be by the action of concentrated hydrochloric acid on sodium or potassium bichromate, but in performing it in this way care in allowing the action to proceed vigorously for two hours I found the chlorine to contain a trace of some gas which was neither taken up by the antimony nor absorbed by the caustic potash. ~~However~~ The amount

of this gas was ~~twice~~ between one and two cubic centimeters and a correction of 1.5 cc in the decomposition trays was applied.

Below I give an average of five determinations.

CO absorbed	CO collected	CO altered	% Change
63.2 cc.	62.4 cc.	0.8 cc	1.26
54.1 "	52.0 "	2.1 "	3.88
69.0 "	68.4 "	0.6 "	0.86
78.6 "	76.6 "	2.0 "	2.54
77.2 "	73.1 "	4.1 "	5.31

From this results it would seem that there is a slight reaction between the two gases, but if the action would be of unusual activity, I am sure we should expect a greater change. My

The above figures indicate.

Action of Hydrogen on Deuteronyl hypochloride

Inasmuch as oxygen has the power to decompose the compound every red and below 0°C., it seemed advisable to try the action of hydrogen, thinking that if the hydrogen did decompose it would result in the formation of deuteronic hydride to be formed.

The compound was prepared in the usual manner and the bulb containing it, still immersed in ice water, was introduced into a system of receptacles similar to that described for [illegible]. The hydrogen was prepared by the action of hydrochloric acid on zinc and was [illegible]

cannot stop [illegible] acetate in potassium permanganate. The hydrogen was bubbled through the compound (at 0°C) for eight hours and at the end of this time the crystals were in no way changed from appearance.

The water contained in the wash bottles through which the gas passed to remove the weak caustic contaminations of compound, was examined carefully; no lead sulphide was found, and was extracted in nitric acid but not silver. Dollens solution in the cell.

The bulb containing the dry borax cupram chloride was finally allowed to assume the room temperature, when the water was slowly given off and later the bulb was heated to 60°, but no change

in the carbon monoxide could be detected.

Action of Nitrogen.

These experiments were conducted exactly as in the case of hydrogen, at 0° the compound was not affected by the nitrogen, and on heating the tube was warmed so that the carbon monoxide was given off, no change whatever could be detected in the latter.

Action of Acetylene on Carbon Monoxide

When acetylene is introduced into water for the purpose of enriching it, a proportionately large amount of the former had to be introduced before the

flame shows any luminosity whatever.

Ammoniacal cuprous chloride will have a series of two unsaturated compounds, each of them having two unsaturated valencies; since acetylene is also an unsaturated compound and to exactly the same extent as the two compounds just mentioned, it seemed possible that carbon monoxide and acetylene might unite under certain conditions and in this way the difficulty experienced in purifying water gas with acetylene be explained.

Suffice it to say that all results obtained were distinctly negative. Measured volumes of carbon monoxide and acetylene were

mixture over mercury and allowed to stand for a week at the ordinary temperature exhibits no change in volume. The mixture when passed through an ammoniacal solution of cuprous chloride precipitates the characteristic copper carbide and the entire amount of gas can be absorbed by cuprous chloride.

A similar mixture passed through a heated tube, suffers no change except that due to the action of heat on acetylene.

The passage of acetylene into dicarbonyl cuprous chloride, or a mixture of acetylene and carbon monoxide into cuprous chloride, or treatment of a mixture of copper carbide and chlor-

bonyl cuprous chloride with hydrochloric acid, are just to effect a union of acetylene and carbon monoxide.

Some experiments were conducted to determine just what proportion of acetylene is necessary to render a carbon monoxide flame luminous.

Mixtures of the two were made and burned from a platinum tip the proportion of acetylene being gradually increased until the flame became very slightly luminous.

Experiments were also conducted with mixtures of acetylene and hydrogen, and acetylene and water-gas readers non-luminous by being passed through fuming sulphuric acid, fuel gas below.

The results are these:

C_2H_2 and CO ; 11% C_2H_2 required
C_2H_2 and H ; 7% C_2H_2 required
C_2H_2 and "fuel-gas"; 2.-2.5% C_2H_2 required

The case of acetylene and carbon monoxide is not an unusual one; instead of the acetylene giving the carbon monoxide this latter renders the acetylene flame non luminous, just as hydrogen does any ordinary gas flame. Of course this is not the explanation, but it is in accordance with facts previously noted and so recently discussed by Heumann as far back as 1876.

The nature of the combustion of acetylene and the rôle it plays in luminous flames has recently been discussed quite fully by Prof. Lewes[2], so that

(1) Annalen, Liebig's, 181, 32; 182, 1; 183, 102 & 184,
(2) Proc. Roy. Soc. 57, 450

further discussion of it is unnecessary.

Discussion of Results

Action of Oxygen on Dicarbonyl Cuprous Chloride.

There can be no doubt that when oxygen is passed into this compound even at 0°C, it undergoes decomposition and there is formed simultaneously a small amount of carbon dioxide. This carbon dioxide cannot be due to an impurity in the cuprous chloride, for oxygen passed through the same cuprous chloride, either at 0° or 60°, gives no carbon dioxide whatever. Further it cannot be due to a peculiar activity of the oxy-

brought about by the cuprous chloride through its oxidation thus causing a splitting of the molecule into atomic or "active" oxygen, for when a mixture of carbon monoxide and oxygen is passed through ferrous sulphate or chloride these compounds are oxidized yet none of the carbon monoxide is converted into carbon dioxide.

Plainly then the oxidation of carbon monoxide by the action of oxygen in dicarbonyl cuprous chloride must be due either to the activity of the carbon monoxide or else it must in some way be brought about through the agency of the cuprous chloride.

While we have some evidence pointing to the fact that both elements and compounds are usually re-

live at the moment of their li- ra-
tion, yet it is far from conclusive
That this activity is a property of the
element or compound per se. Certain
heat phenomena are involved in all
chemical reactions and in some in-
stances at least electrical phenomena,
so That an explanation of the real
or apparent activity of the "nas-
state" must be at present very
much involved.

In the experiment under discussion
one point should be noted especially; if
The formation of carbon dioxide is a
result of the oxidation of the carbon
monoxide on account of its activity,
Then it is very surprising That Volu-
me, which unites with carbon mon-
oxide with some ease, does not do so

to a much greater extent under these conditions and yet it does not.

Plainly then, to explain Lambert's law in its measure to only one of many phenomena and it may ask us all to many assumptions (what part is played by the cuprous chloride, or the products of its oxidation which are necessarily present.

Drehschmidt has shown[1] that when an ammoniacal solution of cuprous chloride is used for the absorption of carbon monoxide, a coating of metallic copper is formed over the absorbing liquid, due, as he thinks, to a reduction of the cuprous chloride by the carbon monoxide.

Further Winkler shows[2] that caustic potash causes the precipitation

(1) Ber. 21, 2?
(2) Zeit. anal Chem. 28, 272

of metallic copper forms a solution of cuprous chloride containing carbon monoxide; carbon dioxide is formed at the same time. Hamilton also points out[1] that by the action of carbon monoxide on a solution of cuprous chloride and palladium chloride there is a precipitation of palladium and formation of carbon dioxide, thus

$$PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl$$

It also shows that carbon monoxide acts very slowly on a solution of palladium chloride, the cuprous chloride facilitating the action very considerably.

I wish to recall here that in the decomposition by means of a current of dicarbonyl cuprous chloride dissolved in water, there was always the

[1] Ibid 28, 274

caused a slight black coating on the flask during the appearance of metallic copper and giving the copper test. A like reaction to that was observed in the decomposition by increased temperature of the compound formed by the absorption of carbon monoxide by cuprous chloride in pyridine. Though in this case it is possible that the pyridine exerted a reducing influence as well as the carbon monoxide.

I have frequently noticed as no doubt have others, that, when strong hydrochloric acid is added to cuprous chloride, the latter turns black and, when this is used to absorb carbon monoxide, it becomes darker until this official effect is probably more

by the bright crystals of the orange cuprous chloride formed.

Phillips has shown[1] that by the action of carbon monoxide on solutions of the chlorides of palladium, iridium, platinum and gold at the ordinary temperature, and on a solution of rhodium chloride at 100°C the metals are precipitated and carbon dioxide formed.

Berthelot[2] has shown, and it has been confirmed by Phillips[3] that when carbon monoxide is passed into an ammoniacal solution of silver nitrate at the ordinary temperature, metallic silver is deposited.

Looked at in the light of the periodic law these facts are of unusual interest. Copper belongs to the

(1) American Chem. Journ. 16, 272
(2) Ann chim phys. [6] 24, 132
(3) loc. cit.

same sub groups as do silver and gold; now the peculiar transitory traits first begin for copper (63) and acting as a kind of connecting link between members of the 4th series and those of the 5th series, comprising iron (56), cobalt (59) and nickel (59), of which both iron and nickel form compounds with carbon monoxide. Again the transitional group ruthenium, rhodium (103) and palladium (106) connects the 6th series with the 5th. The first members of the latter being silver (108); notice that carbon monoxide quickly reduces potassium methenate to metallic ruthenium, also reduces rhodium chloride at 10° and palladium chloride at the ordinary temperature, it also reduces the ammoniacal silver nitrate solution

Passing however to the Transition groups vanadium V, niobium V, tantalum V, platinum VI, connecting the 10th and 11th series, the first member of the latter being gold III. Carbon monoxide quickly reduces osmic acid and also reduces the chlorides of vanadium, platinum and gold to the metals, carbon dioxide being formed.

Of all the metals comprising the Transition groups Ir, Os, Ru, Rh, Pt, Pd, Au, Ag, Hg, those of them compounds, especially the chlorides, are reduced by carbon monoxide, carbon dioxide being formed with the exception of cobalt and nickel and indeed the distinction of uniting with carbon monoxide. Of the sub-groups Cu, Ag, Au, the nitrate of silver is

easily reduced as is the chloride of gold, the chloride of copper being the only exception. Notice further that this peculiar behavior under the influence of carbon monoxide at ordinary temperatures, is confined almost, if not entirely, to these metals.

Of course, we cannot reason conclusively from relations brought out by the periodic law, yet this law does lend quite a degree of probability, in conjunction with the experiments of Bonchschmidt and Mühler, as well as the phenomena described by me. Especially is the probability increased when we are forced to explain the formation of carbon dioxide by the action of the carbon monoxide on clay

The influence exerted by the cuprous chloride. I think one ought to be inclined to reject the reaction as Mulder has shown in the case of palladium chloride. $PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl$ and correspondingly $Cu_2Cl_2 + CO + H_2O = Cu_2 + CO_2 + 2HCl$

The Constitution and Chemical Nature of Dicarbonyl Cuprous Chloride.

As regards the constitution of this compound I have no suggestion to offer. Formulae might be written to satisfy all the bonds of the elements involved, but there is no experimental basis for such a procedure and it would add nothing to our knowledge. It seems fairly certain that

its composition is represented by the formula $Cu_2Cl_2.2CO.4H_2O$, assuming that both cuprous chloride and carbon monoxide are unsaturated compounds it seems only reasonable that they should be able to unite and mutually saturate each other, but how the parts are joined together is a far more difficult problem.

What is still more important under the circumstances, and as regards which I think there is at least some weighty evidence, is a consideration as to whether the so-called compound is in reality a true chemical individual, an "atomic" compound. So far as appearances are concerned, the crystals have

seemingly homogeneous and [illegible] to crystallize in constant crystal form and lustre - Even pure [illegible] would be resolved to some law of its chemical individuality. The compound is quite stable at low temperatures in the absence of active substances, but if the temperature be elevated [illegible] the mercury gradually released at ordinary temperature.

While the term "molecular compound" would most accurately [illegible] applied to this compound some [illegible] a term that is [illegible] but more [illegible] to designate [illegible] of the cause of a certain instability observed in some compounds - yet since at the

present time there is at least some reason to set apart certain compounds as differing from the true atomic compounds. I cannot but feel, judging from the utterances of both books and journals, that some chemists will be inclined to place this compound in that category.

It may be well to recall just how the term "molecular compound" came into use, the conception that is responsible for its existence, the use it has rendered to the advancement of our science and finally to consider the ground on which it now stands, that we may see whether it has any true meaning and value at present.

The conception of "molecular" as opposed to "atomic" compounds was for

outcome of the conception of the atomic capacity of elements and the necessary result of the idea of constant valency. During the development of the type and radical theories in the first part of the century, it was repeatedly pointed out that in all cases of substitution a definite number of atoms of the one element is replaced by a definite number of atoms of the second.

Dumas in 1834 had pointed out that in the substitution of hydrogen by chlorine, one atom of the former is replaced by one atom of the latter, while two atoms of chlorine are required to replace one atom of oxygen.

Indeed the four fundamental types [illegible]

seriously in the same direction, the valency rising from one to four in the order in which they are given

$$Cl\{H \quad ; \quad O\{\overset{H}{H} \quad ; \quad N\{\overset{H}{\underset{H}{H}} \quad ; \quad C\{\overset{H}{\underset{H}{\overset{H}{H}}}$$

Further, the different replacement values of metals were brought out by the classic work of Graham on the phosphoric and arsenic acids, and also by Liebig in his work a little later on the dibasic organic acids. The general significance of these facts was not realized, however, at that time, and we may say that our conception of valency dates from the appearance of Frankland's paper, "On a New Series of Organic Compounds Containing Metals." He showed that while one has the power to form two series of compounds, yet

[1] Phil. Trans. 142, 417

A Triethylamine Et_3N or oxide of ethyl
ene diamine $Et_2N_2H_2O$, the two
latter assuming to be saturated and the
compound may be looked upon as
Et_2O, one atom of which has been
replaced by $(CH_3)_2$.; similar results
were obtained with other organo-metallic
derivatives. From a comparison of the
oxides, chlorides etc of phosphorus, arsenic
antimony and nitrogen, Frankland
shows the tendency of these elements
to unite with other elements in com-
pounds of three or five atoms of the
uniting Elements. Then [illegible] that
Frankland assumes a saturation ca-
pacity of the elements, the limit in
the cases cited by him being reached
by the number 5. However he did
not suppose that the elements have

a constant valency; his idea was that although valence was variable, as could be seen in the compounds SnO_2, SnO, yet in every case there is a limit, and while in the case of PCl_3 the structural capacity has not been reached, yet there is a limit, and this limit is reached, as he thought, in the compound PCl_5.

It is but fair to state that the work of Kolbe, a little later, had a good deal of support which was not at that time available, and he was the first to make use of the term 'saturation value'. It showed that both these methods have been replaced by values and notations of the type we find Fe'' and Fe''', Sn'' and Sn'''', still in use.

These ideas were not established during the fifth decade, such elements

as Erlenmeyer [illegible] Kekulé and Kerkuvé [illegible] there, and [illegible] while was [illegible] have as a saturated compound, a compound in which all of the valencies of nitrogen are expressed; ammonia was considered just as truly a chemical compound, except in this instance only three of the five nitrogen affinities come into play, the compound thus being unsaturated.

In the year 1857 Kekulé[1] introduced the conception of mixed types, a modification of the condensed types of Gerhardt and in 1858 he published his theory of valency[2], introducing the [illegible] and established his doctrine of "Linking or Atomicity"

(1) Annalen der Chemie 104, 129
(2) Ibid. 106, 129

Kekulé's views underwent a gradual growth as can be seen from his papers in Liebig's Annalen during 1857, '58 and '59 and culminated in his famous Lehrbuch der Organischen Chemie which began to appear in 1859. One can well see how that all the work of Kekulé from that on the subject now rests to that which led him to the conception of the linking of atoms, brought him, by a peculiar combination of facts, to believe that the valency of elements is constant, and indeed "he declares" it to be as unalterable as the atomic weights.

This led to quite an animated discussion during the years 1863, &c. between Kekulé and Hemp, Report

(1) Compt. rend. 58, 510

and others. Similar looking are trogen and phosphorus as only smaller sulphur and oxygen bivalent etc. and in order to explain the compounds NH_3, PCl_3 etc. he was forced to assume a fundamental difference between NH_3 and PCl_3, and NH_4Cl and PCl_5. The former he named "atomic" the latter "molecular" compounds. It was known that the vapor densities these latter compounds were of one in relation the first and the criterion by which he judged a compound to be atomic or molecular was its stability or instability to be converted into the gaseous state without decomposition. He claimed that in the atomic compounds the component parts are held together by the attraction of

of the individual atoms; this might be termed the intra-atomic force. The molecular compounds, on the other hand, were supposed to be made up of two or more individual molecules, which were held together by inter-molecular rather than an intra-atomic force, which, however, is sufficiently strong to preserve the union under the ordinary conditions.

It can be seen at once how artificial and meaningless such a division of compounds must have proven to be, and it is not unnatural that great opposition was encountered. That this was the case can be seen from the articles of Nölbr" and Naquet's. One sentence from the paper of Nölbr, just referred to, is worthy of

1) Journ. prakt. chem. (2) 2, 260
2) Compt. rend. 28, 38

refutation, since it approaches the case so admirably; speaking of molecular compounds he adds, "Es ist, in der That, ein Wort und es sounds very learned, however it is only a word, as that of which the fool says: 'Es ist mir Begriffe gestohlen, du, stellst mir Nicht zu rechter Zeit auch ein.'"

Yet in spite of all the assertions that were strewn out against the existence of molecular compounds into the "atomic" and "molecular" regions, in spite of the convincing proofs that such a procedure is unwarranted, just the same there has crept into the minds of some chemists a belief that there is an internal difference in structure in some compounds, just as if such [illegible]

jected - a difference supposing proof in case of decomposition. True, great case of decomposition, e.g. under the influence of heat, must be an evidence of comparative instability in the compound when heat changes are involved, but does this justify one in calling such a compound "molecular"? Yet this is exactly what is not infrequently done, in proof of which I have only to refer to the often quoted book of Naumann "Die Molekülarveränderungen nach festen Verhältnissen" Heidelberg 1872 in which he makes exactly the same distinction as did Rebuffat few years previously, or to come to the immediate present I cite the "Lehrbuch der Chemie" of Meyer and Jacobson[1] in which they

[1] Vol. I pp 58, 59

term the compound formed by methyl ether and hydrochloric acid molecular, being made up $(CH_3)_2O.HCl$. And just as until very recently the so-called "double halides" were considered molecular compounds and even now the salts containing water of crystallization are quite frequently placed in this class!

The survival of this conception was due probably in the first instance, to the fact that it was put forward by Kekulé and incorporated in his "Lehrbuch", and naturally the great brilliancy of his work, as regards the structure and relations of organic compounds, gave great and lasting impetus to the conception of molecular compounds. Then too the book of Naumann just referred to, and

something to sustain the idea; but more potent than all else was that peculiarity of human nature which is the evident by recognized – a strong tendency to substitute a term for lack of knowledge and thus lull the conscience to rest and finally to be so accustomed to consider the term knowledge.

The state of chemical knowledge happened to be peculiarly adverse for progress in the ideas put forward by Kekulé. It so happened that not a single compound was known, in which a valency seemed to be greater than that granted by Kekulé, but also there was an abnormal vapor density, and many of the proofs we now have were then lacking.

Two of the cases especially cited by

Kekulé uses the abnormal vapor densities of ammonium chloride and phosphorus pentachloride, the irregularity observed in the densities of these compounds was assumed to be due to their decomposition when converted into vapor;

$NH_4Cl \rightarrow NH_3 + HCl$, and $PCl_5 \rightarrow PCl_3 + Cl_2$

This assumption received absolute proof when in 1862 Sebal succeeded in separating the vapor of ammonium chloride into ammonia and hydrochloric acid. This result was obtained by utilizing the difference in the rate of diffusion, through an porous diaphragm, of the lighter ammonia as compared with the heavier hydrochloric acid.

Similarly, and without the use of a porous diaphragm, Wurtz

(1) Annalen der Chemie 123 187

Two objections to Hinshelwood and Robinson's[1] suggestion as explaining the reactions between sulphuric chloride and ferric chloride and chromic chloride at temperatures of 300°C. The diffusion taking place in an atmosphere of carbon dioxide. It is interesting to note that the same experiments have succeeded in separating sulphuric acid into sulphur trioxide and water by means of the same method, the temperature being in this case 445°; surely sulphuric acid is a true chemical compound.

We doubtless owe much to Graham and to the conception that in the molecule chloride and perchloride of iron the affinities of the nitrogen are stronger than the

[1] Proc. Roy. Soc. 12, 510

other two, in the former instance and that in the latter case the same holds true for the attached phosphorous

That the two constituents have a difference of internal structure as claimed by Kekulé, was very ingeniously shown by Meyer in 1864 by the use of a substituted ammonium chloride. One of the compounds thus made use of was dimethylethylamine monium chloride; plainly if there is any difference in the relations which these constituents have to the nitrogen atom, then the compounds made in this way

$N(CH_3)_2 C_2H_5 + C_2H_5 Cl = N(CH_3)_2 (C_2H_5)_2 Cl$

should differ from the one made thus

$N(C_2H_5)_2 CH_3 + CH_3 Cl = N(C_2H_5)_2 (CH_3)_2 Cl$

However, not the slightest difference

* Annalen der Chemie 132, 173

was found and the same result was
reached in the case of many substituted
ammonium chlorids that I have
studied. There is no doubt that in these com-
pounds nitrogen is pentavalent and
the decomposition is exactly analogous
to that of ammonium chloride:

$$NH_4Cl \rightarrow NH_3 + HCl$$

and $NR_4Cl \rightarrow NR_3 + RCl$

It is but fair to state that the
question has been raised by Lossen and
with some reason whether the meth-
ods employed by myself and Lossen
sufficiently guard against such
slight differences in constitution as
might be caused by a difference in
the affinities of the five atoms of the com-
pound as compared with the other
three.

(1) Annalen der Chemie 181, 364

Utilizing the same procedure as that employed by Meyer and Press[1], Collie[2] has shown that in the substituted phosphonium compounds all the organic radicals have the same relation to the phosphorus atom. For example he found that di methyldiethyl phosphonium iodide as prepared either from trimethyl phosphine and ethyl iodide or from diethyl phosphine and methyl iodide

$$P(C_2H_5)(CH_3)_2 + CH_3I = P(C_2H_5)(CH_3)_2 \cdot CH_3I$$

and $$P(CH_3)_3 + C_2H_5I = P(CH_3)_3 \cdot C_2H_5I$$

In 1873 Thorpe[3] prepared phosphorus pentafluoride which is gas, and its density agrees with that required by the formula PF_5. This work has been confirmed by Moissan[4], the mean of

(1) loc. cit.
(2) Journ. Chem. Soc. 23, 717
(3) Chem. News 32, 232
(4) Compt. rend. 112, 1199

vapor density determinations being 7.42
That required by PH_3 being 7.40

Further Baker[1] claims that the
vapor density of absolutely dry ammonium
chloride is not abnormal at a
temperature of 350°; The mean of two
determinations being 27.8, while That
required by NH_4Cl is 26.75. If however
the least trace of moisture be present the
value drops at once to 13.2 – 13.9.

I do not see how these results can have
any bearing on the distinction made by
Kekulé, between molecular and atomic
compounds. However, some may find
that a compound That is decomposable by a reduction of pressure may
in some way differ from a true chemical compound; the marked effects of
heat changes are so apparent as not

(1) Jour. chem Soc. 65, 615

to be mistaken, if the effect produced by pressure changes are less common and as relevant as I look for, on the account I have to give of the properties of the compounds of carbon with hydrogen.

Effect of Pressure Changes on the Molecular Weight of Compounds

It has been observed by Naumann[1] that not only does the density of acetic acid vary with the temperature but also with the pressure, the temperature remaining constant. One series of determinations will suffice to show this

Acetic Acid Temperature 100°

Pressure	Density	Pressure	Density
373 mm	3 44	238 mm	3 1
342 "	3 31	232 "	3 2

[1] Annalen d. Chemie 154, 305

Pressure	Density	Pressure	Density
186 mm	3.06	130 mm	2.94
168 "	3.01	92 "	2.76
156 "	2.98	78 "	2.66

Thron heal for $C_2H_4O_2$ = 2.093

" " $C_4H_8O_4$ 4.180

That these results are not confined to this temperature is shown by the fact that similar results were obtained at temperatures ranging from 18° to 183°. This work is confirmed by that of Ramsay and Young, results of the same order being obtained through a much wider range of pressures.

Quite an interesting example is that of hydrofluoric acid. The molecular weight as determined by Gore corresponds to the formula HF. Dr. 188 Mallet determined the density of the vapor of this acid at 30°. By

1 Jour. Chem Soc
2 Ibid.
3 Amer Chem Jour

...ygbing bromoy ...olumes of its vapor ... obtained 3.32 for the molecular weight, ... ing almost exactly with that required by N_2t_2.

By a still more extensive piece of work Thorpe and Hambly[1] show that ... the ordinary temperature the compound is to be expressed by the formula H_2 ... By lowering the temperature the molecule becomes more and more complex until at ... reaches N_2t_3, and this change is gradual, then brings us breaks in the ... curve showing this variation. To reverse this, an elevation of temperature exhibits a decrease in volume and they found that a decrease of pressure exerts a similar influence, as can be seen from the following series of determinations

[1] Journ. Chem. Soc. 53, 765 and 55, 163

Temperature	Barometer	Vapour tension	Grams water
32.0°C	743 mm	19.8	39.74
32.2°	686'	17.89	35.78
32.8'	630'	16.77	33.98
32.0°	603'	15.4	30.82
32.5°	545'	13.85	27.78
32.3°	478'	13.27	26.54
32.7°	354'	11.50	23.00
32.5°	353'	11.37	22.78

The case of nitrogen peroxide is of the same order. Naumann has shown that for any temperature the dissociation of N_2O_4 into $2NO_2$ is the less the pressure, as these two cases show:

Temp. 18.0°C and 279 mm pressure dissociation = 17.5%

18.5° and 136" " " = 29.5%

Again Temp. 20.0° and 280' " " = 17.8%

" 20.8° and 153' " " = 29.3%

1) Ber. 11, 2045

One of the most peculiar cases of [illegible] that first noticed by Bohr. If how a given mass of oxygen is enclosed in a tube and the pressure reduced to about a one millionth of a millimetre of mercury the volume of gas tends to increase as though some of the molecules had begun split into smaller particles. The same phenomenon has also been noted by Baly and Ramsay and also by G. Bredig[2], but no satisfactory explanation as been reached.

The Dissociative Influence of Reduced Pressure on Chemical Combinations.

One of the most striking instances of this kind is the effect produced by reduced pressure on the dissociation of hydriodic acid as shown by the work of Lemoine. The means provided available had to be

(1) Phil. Mag. [5] 38 326
(2) Phil. Mag. (1894), [5] 38 326
(3) A Contribution to the Study of Dynamic Isomerism (1899)
(4) Ann. Chim. Phys. [5] 12 145

with constant temperature. The less the pressure the smaller the amount of hydrogen and iodine in combination.

[illegible] at 440° C.

Pressure	% of formed hydrogen
4.5 Atmospheres	24 %
2.3 "	25 %
0.9 "	26 %
[illegible]	[illegible]

Similar results were obtained at 26° and 350°.

A notable striking example is furnished [illegible] The reaction [illegible] is almost [illegible] at 450° hydrogen dioxide being formed, yet if the pressure be three [illegible] 24 [illegible] of the [illegible]

W. Ann. Chim. Phys. [5] 19, 464

off again; in other words, by means of a reduction of pressure at [illegible] this transformation $BaO_2 \rightarrow BaO + O$.

Theory of Deacon's Process to Retard Decomposition.

One of the most successful [illegible] this nature is the work of Debray [1] on the decomposition of calcium carbonate, which was confirmed a little later by Mallard [2]. But in these [illegible] that at a temperature [illegible] there is a decomposition, not always definite, [illegible] calcium carbonate be heated [illegible] closed vessel, carbon dioxide will be given off until a certain pressure within the vessel is reached, and then the decomposition will cease, and if the

1) Compt. rend. (1867) 64, 603
2) Ann. des Phys. Pogg. 129, 217

known to sufficient increased calcium
carbonate may be melted without de-
composition.

D'Ans[1] has found the same to
hold true for barium carbonate, and
indeed the same author has studied the
limiting pressures of about a dozen of
the compounds of the alkali metals with the
metallic halides formally similar
ular and the carbonates
actly like calcium carbonate.

Some progress has been made in
the study of inorganic salts containing
water of crystallization, by a study of the
transformation of their compounds. Some
surprising results have been obtained by
Debray[2] from a study of the limiting
pressures of dissociation of
Cases such as

(1) Compt rend 86, 332
(2) ibid. (1868) p. 194

Tab. I. 16.

Temperatur	Limit Pression	Temperatur	Limit Pression
12.3°	5.- mm	31.5°	30.2 mm
16.3°	7.1 "	30.4 Salt melts	31.3 "
20.1°	13.1 "	32.0°	37.0 "
24.0°	18.2 "		

Wiedemann has studied the dissociation of the following compounds; $H_2SO_4.H_2O$; $FeSO_4.H_2O$, $CuSO_4.2H_2O$, $CuSO_4.H_2O$ and $FeSO_4.H_2O$. For each temperature a limiting pressure was observed, the result being quite similar to those obtained by Debray with calcium carbonate, except in that case when the salt is capable of forming more than one hydrate.

True this may be a very slight beginning, but it is a legitimate

(1) Ann der Phys Pogg. (1874) 474 and Journ f. prak. Chem 9, 1 (1875)

toward the solution of the question as related to the constitution of Ferric Compounds.

Effect of increase of acid constituent in the decomposition of compounds.

Among reasons for the decreasing effect of reduced pressure and the opposite effect of increased pressure let us see one case which shows the effect of an excess of one constituent, in this way the partial pressure of the constituent present in smallest amount is reduced, undergoes a considerable reduction of pressure. This is true in the work of Lemoine on the dissociation of hydriodic acid, but one of greater theoretical interest is that of the nitrogen carbamate. As was previously stated

by the work of Rayman, [illegible]
he confirms the much earlier work
[illegible] Ammonium carbamate is converted
into vapor it undergoes dissociation
into ammonia and carbon dioxide,
the amount of dissociation varying
with the temperature. Working at re-
duced pressures the results are as follows:
dissociation is greater in a vacuum
than in the presence of one of the con-
stituents and the greater the pressure
of this constituent, temperature remain-
ing constant, the less the dissociation.
For each temperature there is one step
pressure and the limiting pressure
is greater the greater the temperature.
There is an excess of carbon dioxide
than when ammonia is in excess.

(1) Brv. 44, 779

I mention this case in as the decomposition was by me there was an excess of carbonic acid.

Effect of Salts on Dissociation Tension.

Finally I desire to refer to the effect of solvent on the dissociation tension of a compound; the work of Gautier furnishes an excellent example. He finds that pure dry acid sodium carbonate is not perceptibly dissociable below 25°C in a vacuum. However it is very slightly dissociated in a vacuum of 10 – 20 mm at 25 - 30°C. In a vacuum

Original weight $NaHCO_3$ 4.4711 gr
Weight after 48 hours 4.4748

0.0029

If the temperature be raised to 110 - 115° dissociation is almost complete,

Bull. Soc. chim. 26, 115

The same material was used for all the following experiments.

Original weight of $NaHCO_3$		1.2667 gr.
Weight after 2 hours	100° in a vacuum	= 1.1761
" " 8 "	" "	= 0.9900
" " 20 "	100-110° "	= 0.7767
" " 48 "	100-116° "	= 0.7956
Loss in weight		= 0.4711
Loss required by $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$		= 0.4478.

The presence of water causes the entire difference in amount. A known amount of acid sodium carbonate was dissolved in 20 grams water and the solution placed in a vacuum of 300-400 m.m. at 25-30°, and the rest of four days. The salt was dry; the mixture contained about 18.7 % of $NaHCO_3$ and 81.3 % Na_2CO_3. The amount of water present affects only materially the rate of decomposition of the salt in any mixture the temperature

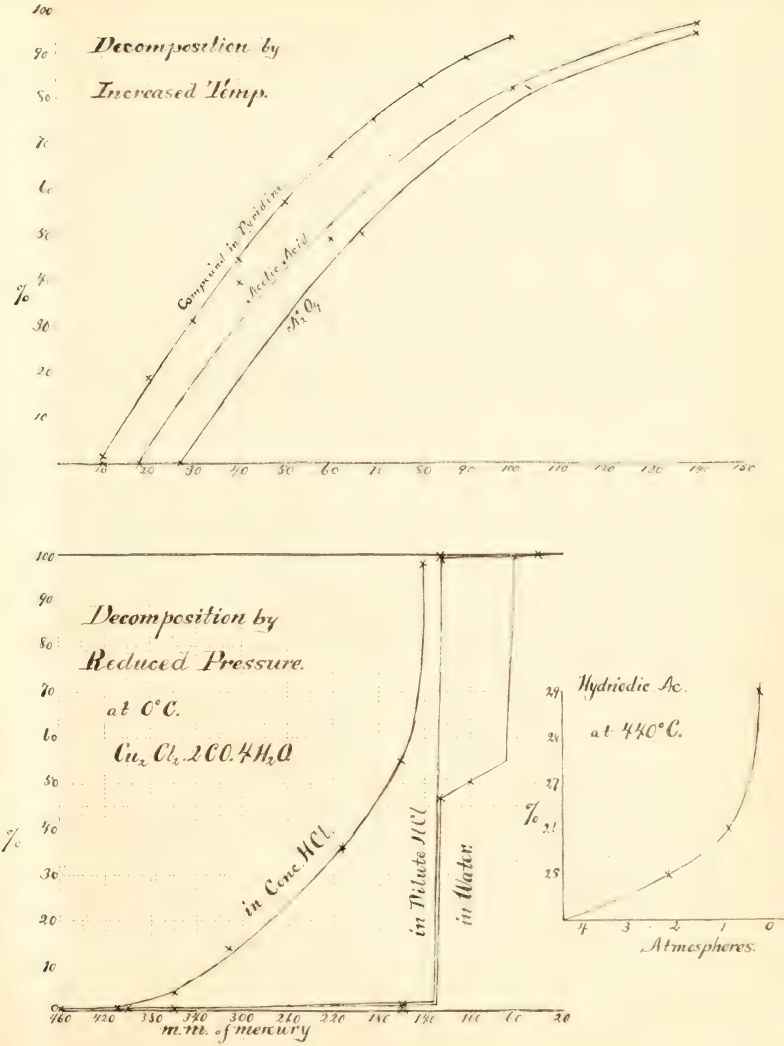
tion is practically nothing being only 2 to 3% instead of 81.5 when 20 grams of water are used.

The effect of water on the dissociation of acid potassium carbonate is exactly similar to that recorded on the sodium salt. Also Berthelot and Ogier found[1] that dry acid ammonium carbonate suffers almost no dissociation but in the presence of water or water vapor the tension is very markedly increased.

Let us consider again now the behavior of dicarbonyl cyanamide when under reduced pressure and also when it is submitted to increased temperature.

As regards the ~~The~~ behavior under reduced pressure: [illegible]

[1] Compt. rend. 103, 665 and 716


Decomposition by
Increased Temp.
%
Compound by Pyridine
Acetic Acid
$Ar_2 O_3$
Decomposition by
Reduced Pressure.
at 0°C.
$Cu_2 Cl_2 2CO.4H_2O$
%
in Conc. HCl.
in Dilute HCl
in Water
m.m. of mercury
Hydriodic Ac.
at 440°C.
%
Atmospheres.

ways it conducts itself quite differently. In that instance in which carbon monoxide is absorbed with most difficulty (use of pure water), it is most difficultly given off by a reduction of pressure, and in that instance in which it is most easily absorbed (by use of hydrochloric acid), it is most easily given off. The compound made with dilute hydrochloric acid decomposes almost entirely at one point 130 mm pressure. The break observed in the decomposition of the compound made with water is probably somewhat exaggerated in the curve on page 1336, though it is undoubtedly in something of a break, yet it extends only through a very short range of pressure-points, about 130 to 160 mm so that in any

slight error in observation would lead to quite different results. I hardly think this slight irregularity, extending through only 30 m.m. a sufficient reason for concluding that in the compound made with water, when we seemingly have a splitting off of one half of the carbon monoxide and then the rest, that of the two molecules of carbon monoxide in the compound, one molecule is united in a manner different from the other.

When concentrated hydrochloric acid is used, the decomposition is of quite a different kind, due most probably to the fact that in this instance portion of the compound is in solution. Just how this could bring about such a change in course of reaction

can known, but that the presence of a solvent does have a marked effect was shown in the work already cited on the dissociation of the acid carbonates of the alkalies. These substances show almost no tendency to decompose at the ordinary temperature, more only little by little to about 100° when it is entirely decomposed within a few degrees; just as decomposed mercuric chloride decomposes in a tube sealed only very slowly until a pressure of 135 mm is reached and then it is entirely decomposed with very little variation in pressure.

However the acid carbonates when moist decompose slowly at the ordinary temperature showing the first effect produced by the solvent

Dr Herr Dr Hoschmidt has pointed out that carbon monoxide which has been absorbed by an ammoniacal cuprous chloride solution can be driven out by passing through the solution an indifferent gas, as nitrogen. On the other hand, I have found that when nitrogen or hydrogen is passed for eight hours through water in which crystals of dicarbonyl cuprous chloride are suspended, the crystals remain the least degree decomposed, provided the temperature be kept, of course, the temperature be slightly raised decomposition will occur.

As regards the decomposition by increase of temperature of the compound in question the absorption of carbon monoxide by cuprous

ride, no further comment is necessary, as it is strictly analogous to the similar decomposition of compounds which must be accepted as theoretic. The truth of this is strikingly shown by a comparison of the curves showing the decomposition of the carbonic acid and the decomposition of hydriodic acid as given shown by the work of Lemoine. The analogous decompositions of iodic and nitrogen peroxide are also to be easily recognized.

The decomposition of dicarbonyl carbonic chloride and the exactly similar decomposition of hydriodic acid by nitric peroxide, when the former is treated hydrochloric acid is so well shown by the curves that nothing further need be said.

In summing up all the evidence of the carbonyl oxychloride I can find nothing which could lead me to consider it as anything else than a true chemical compound. Its definite mass of crystal form, constancy of composition and its behavior under temperature and pressure changes, it conducts itself like a true chemical individual.

The decomposition of a compound by a reduction in pressure is not unknown as I have attempted to show, yet it is unusual. Our conditions of observation are so extremely limited that we are inclined to believe impossible that which is not customary under these limited conditions. But as with chemical compounds, so also with their physical and chemical properties

are concerned, the result of their movement. Do we exclude nitrogen from the list of metals simply because it exists in the gaseous form at the temperature at which we happen to live? Indeed do we not look upon hydrogen, if not as a metal, yet very closely allied to the metals?

Further, do we consider nitrogen and chlorine as being something different from a true compound because under our conditions its parts are so balanced that the least outward disturbance destroys the equilibrium and renders the substance impossible. Not at all, the unusual is not the impossible and yet they are sometimes confused.

Compare our ideas no longer to mere

narrow limits of temperature and pressure, give no other conditions could we shall have other compounds. At the temperature of the sun we should have no solid compounds - water would give no compounds at all; waters of lakes and oceans we should have great volumes of oxygen and hydrogen. At the temperature of absolute zero we should have no gases and certainly many of our compounds would be considered elements. Indeed our compounds are just on the border-land - stable enough to exist but not so stable as to withstand any means of decomposition, and it is this very instability that enables us to class them as compounds rather than as elements.

Can we lay down a rule

ments, can we not say that all the
varied things that we know come out
of these? Have we ~~the~~ known these are
but new interpretations of natural phe-
nomena. Our nature is constant
but our knowledge is incomplete and
our enjoyment often false. With new
facts before us we must modify and
extend new ideas. Else our best
friends will be enemies and blind
our eyes to truths yet to be revealed.

The distinction between hydrogen
returns "molecular" and "atomic" com-
pounds caused longer to hold, any
more than the conception which gave
birth to the distinctive - constant valen-
cy of the elements. I do not wish to im-
ply that all ~~the~~ atoms of the
same chemical order, but I do wish to

Proteus is named for one of the three molecules composing the atom that Kekulé used it. It would only fail to take on any shape but one. The other hand allows no proposition to exist. That we have gotten some insight into a compound makes the inquiring mind want to know further inquiry.

It will be noticeable to see that I have written the formula $Cu_2Cl_2 \cdot 2H_2O$ but not as Kekulé would have written it, and which may simulate to the old established formulae of Berzelius, which conception seems to the minds author of the molecular idea. By these dots I do not mean to imply that between Cu_2 and Cl_2 there is one kind of attraction and between Cu_2Cl_2 and $2H_2O$

There is another, [illegible] not a state of equilibrium in the compound but rather a state of ignorance in ourselves.

I think we can say that in the compound we have the elements in proportions Cu_2Cl_2 and $2CO$ and $4H_2O$ and [illegible] but it might be better to write the formula $Cu_2Cl_2C_2H_8O_6$.

If when we speak of a compound as molecular we mean simply that we do not know how the various parts are arranged as regards one another, well and good, but when we speak of ammonium chloride, for example, as a molecular compound and mean by this that the interatomic forces between the atoms NH_3 and HCl are of different kinds, when

we have our conceptions of the chemical relations of a compound in the usual state or an instability in the gaseous state, and worse than all when we try to explain chemical phenomena by a distribution of names that is subject to the term and believe that progress is founded by such a usage.

Thirty years ago a term was introduced into the chemical language; no doubt it did some good ~~incorrectly~~ as it directed the attention of chemists to a certain class of compounds, and caused them to enquire into the nature of the relations existing in them. A separate class was formed, but one by one these molecular compounds

have been shown to be true chemical compounds until there seems to be only two classes of compounds to be found which the hypothesis of Berthollides conception of molecular compounds can entrench themselves. I refer to the compounds containing "water of crystallization" and the so-called double halides. Both of these contain what might be called conception compounds of the latter class are fast losing their mysterious chemical status, and are a few notable instances there of the former class have received the same treatment. I refer especially to mesocalic acid and chloral hydrate.

We see at once that real advancement has been made along these

times, and let us hope that the future may give us insight for keeping these wild passions, knowing that, when these territories once so dark, shall have been not only explored but taken full possession of by chemists, that larger lands will attract our attention, deeper problems will confront us; but with the new implements in our hands, which each succeeding year brings to us, and brought by the heirs of those who have gone before, aided by a casting off of all useless armour and hampering us and simplified by the wisdom of the past, we shall attack the new problems with a renewed vigor and thus the progress of things

will go on and use for the broad-
ening of our science and the ad-
vancement of man.

Inorganic compounds containing carbon monoxide

Since the product of decomposition
cuprous chloride magnesium is meant
many researchers it may be
well to note briefly the other inor-
ganic compounds containing carbon
monoxide and to see if we can de-
duct any generalities belonging to
these as a class.

$COPtCl_2$ Schützenberger Ann chim phys [4] 12/350
and ibid [4] 12/350

$(CO_2PtCl_2$ "

$(CO)_3(PtCl_2)_2$ "

$(CO)^1Pt^2H_2O_2$ Sullivan Chem N 53
and [illegible]

$CO\,Pt\,R_2 \cdot 2HCl$ (R = primary base) Compt. rend 126, 128

$CO_2\,Pt\,(NH_2\cdot)_2 \cdot 2HCl$ etc "

$CO\,Pt\,Cl_2 \cdot C_5H_5N \cdot HCl$ Jacobsen Ber. 22, 2921

$CO\,Pt\,Cl_2 \cdot C_9H_7N \cdot HCl$ etc "

$CO\,Pt\,Br_2$ "

$CO\,Pt\,I_2$ "

$CO\,Pt\,Br_2 \cdot C_5H_5N \cdot HBr$ etc. "

$CO\,Pt\,CNS \cdot KCNS$ "

$CO\,Pt\,S$ "

$CO\,Pt\,O_{(?)}$ "

$(CO)_2\,Pt\,Cl_6$ or $Pt\,Cl_2 \cdot 2\,COCl_2$ Hallinger & Chem. Soc. 38, 98 and Ber. 24, 2291

$CO\,Pd\,Cl_2$ Dennis Compt. rend 126, 646

$(CO)_2\,Pd\,Cl_2$ "

$(CO)_3\,(Pd\,Cl_2)_2$ "

$Ni\,(CO)_4$ Mond Langer and Quincke J. Chem. Soc. 57, 749 and Chem. News 64, 108

Brit. phys. Chem. 8, 50

$Fe\,(CO)_5$ Mond and Langer J. Chem. Soc. 57, 1090

$Fe_2(CO)_9$ Mond and Langer Proc. chem. Soc. 17, 170
$Fe_3(CO)_{12}$ Mueller Compt. rend. 107, 777
and Ann. chim. phys. [6] 17, 91
$Pt_4(CO)_5$ (prepared in many ways) Hartley & Dobbs. Phil. Trans. Roy. Soc. 180
$Pd_4(CO)_5$ " " "
$COCl_2$
COS

To review very briefly some of the properties of these compounds. All of them are more or less unstable and the decomposing tends to give off carbon monoxide as such, unless an oxidizing agent is present, when all or a part of the carbon monoxide appears as carbon dioxide.

Of the gaseous compounds $COCl_2$, COS and H_2CO_3, COS is the most stable at a dull red heat into CO and S.

and at about 200° it CO_2 is decomposed into Pd and CO_2. The other compounds with the exception of $FeCO_5$, undergo decomposition when converted into vapor, the carbon monoxide usually appearing as such and when $FeCO_5$ is broken down at 200-350°.

The compounds $CO\,Pd\,Cl_2$, $(CO_2\,Pd\,Cl_2)_2$ and $(CO_3\,Pd\,Cl_2)_2$ similar to $CO\,Pd\,Cl_2$, $CO_2\,Pd\,Cl_2$ and $(CO_3\,Pd\,Cl_2)_2$ can also be converted one into another by changing the temperature and the proportion of carbon monoxide present, and all of them are decomposed by water in the cold. In the case of $CO\,Pd\,Cl_2$ and also $CO\,PdCl_2$, when decomposed in water all the carbon monoxide appears as carbon dioxide, due probably to the intermediate formation of carbonyl chloride which

as these are acted on by the water. When an excess of carbon monoxide is present as in $CO_2 PtCl_2$, just one half of the carbon monoxide suffers oxidation. These decompositions are

$$CO\,PtCl_2 + H_2O = Pt + CO_2 + 2HCl$$

$$CO_2\,PtCl_2 + H_2O = Pt + CO_2 + 2HCl + CO$$

$$(CO)_3\,PtCl_2 + 2H_2O = Pt + 2CO_2 + 4HCl + CO$$

The corresponding palladium compounds are decomposed in an exactly similar manner.

The compounds $CO\,Pt(NH_2)_2.2HCl$ $CO_2\,Pt(NH_2)_2.2HCl$ $CO\,PtI_2$ $CO\,PtBr_2$ etc are also decomposed by water. When $CO\,PtBr_2$ is heated in an atmosphere of carbon dioxide it is decomposed thus: $CO\,PtBr_2 \rightarrow CO + PtBr_2$.

When a solution of $CO\,PtCNS.KCNS$ is simply evaporated carbon monoxide

ides are free. The compound COS_2 is so unstable that it decomposes in a vacuum.

All of the compounds of the type $CO\!<\!\begin{matrix}O\\ R\end{matrix}$ $CO\!<\!\begin{matrix}O\\ NH_2\end{matrix}$ and $CO_2\!<\!\begin{matrix}NH\\ NH_2\end{matrix}$ and (R = residue of ammonia or any primary base) $CO\!<\!\begin{matrix}O\\ CNS\end{matrix}$ etc are decomposed by the action of potassium cyanide, carbon monoxide appearing as such in every case.

Even from this exceedingly brief review I am sure it will at once be apparent that similarity between dicarbonyl cuprous chloride and the above compounds, a similarity so great that one could not fail to classify it with them as a true chemical complex!

One account of the similarity in composition between CO, Cu_2Cl_2 and

and the compound $(CO)_2 Cl_2$. Also from those in the former compound the source which I have used is Thorpe's - decomposing cuprous chloride, being in accord with the source given to the latter compound by Schützenberger.

Conclusions.

I Carbon monoxide is not absorbed by dry cuprous chloride. It is absorbed by cuprous chloride when this substance is in solution in concentrated or dilute hydrochloric acid or even when suspended in water.

II As a result of this absorption a compound of definite composition is

formed similar in all cases ~~which~~ is to be represented by the formula $Cu_2Cl_2.2CO.4H_2O$.

III. This compound conducts itself like a true "atomic" compound. It is decomposed by a reduction of pressure or by an elevation of temperature, but these decompositions are exactly like the decompositions of other substances, the true "atomic" nature of which cannot be doubted.

IV. Crystals of dicarbonyl cuprous chloride are unaltered at 0°C. by the action of hydrogen or nitrogen. They are immediately decomposed, however, at this temperature, by oxygen or chlorine. It seems that at

cuprous chloride which is the sensitive constituent under the influence of these reagents.

V The carbon monoxide shows no marked increase in chemical activity at the moment of liberation from the compound.

VI From a comparison of cuprous chloride with the other inorganic compounds containing carbon monoxide, it is found to conduct itself in a manner similar to them, and deserves to be ranked with them as a true chemical compound.

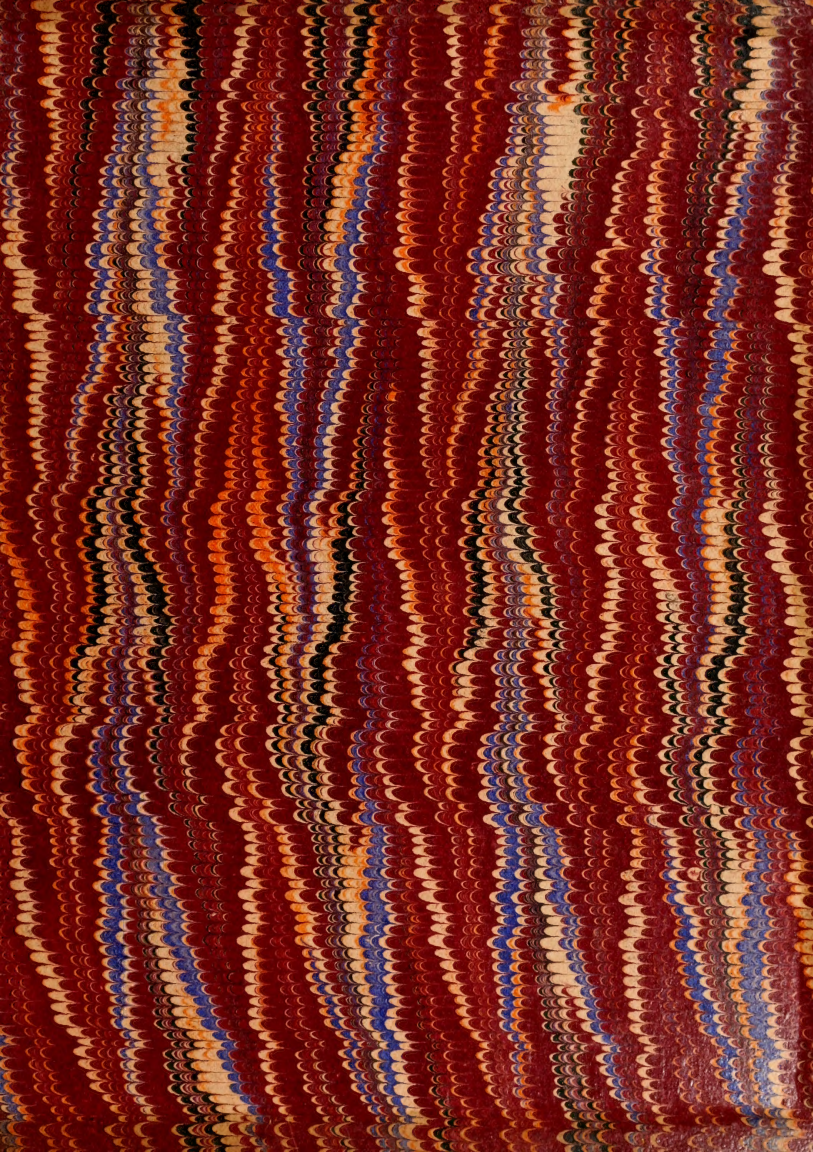
Biographical.

William App Jones was born in Hillsboro N.C., Nov. 24th 1873. His early training was received in the private schools of that place.

In 1886 he entered Moraman Falls Academy, and after three years of preparatory study he entered Wake Forest College (N.C.), from which institution he received the degree of Bachelor of Arts in 1893. After being in business for a year he returned to his Alma Mater where he spent a year in the study of chemistry.

In 1895 he entered the Johns Hopkins University where he has since devoted himself to the study of chemistry, geology and mineralogy.

In the spring of 189[illegible]

appointed a Fellow in Mathematics for the present year and since Jan. 1898 has been acting as lecturer, assistant to Prof. Ramsay.

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